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C-1139 (3-45)

Y-12 CENTRAL FILES

Index No. Y-166

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Issued To: C. R. I. O.

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CARBIDE AND CARBON CHEMICALS CORPORATION

Y-12 PLANT

W-7405-Eng-26

SPECIAL HAZARDS PROGRESS REPORT

April 1 - 30, 1948

Raymond Murray

Oak Ridge, Tennessee
May 11, 1948

[redacted]

Index No. Y-166

[redacted]

Distribution, Series A.

1-2 Mr. C. E. Center
3. Dr. C. E. Larson
4. Dr. P. D. Scofield
5-9. Mr. Ned Williams
10-11. Mr. Raymond Murray
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Central Reports and Information Office
Date Issued:

MAY 1 8 1948

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SPECIAL HAZARDS PROGRESS REPORT
April 1 - 30, 1948

SECTION I: CRITICAL MASS

1. No limit violations, or cassette film exposures in excess of 0.1 roentgen were reported or recorded during April.

2. Calculations and Recommendations on Plant Procedure and Equipment

   a. Issued recommendations regarding limits and conditions for safe storage of consumer parts in

      (1) Birdcages
      (2) Standard Mosler safes
      (3) 9212 Wing D vault

   b. Surveyed X-Ray spectrometer target for activity from yttrium sample prior to use in the XAX X-Ray spectrometer.

   c. Checked high voltage supply to XAX spectrometer for X-Ray production by use of film.

   d. Surveyed beam probe located in experimental tank, track 6, 9204-3. Made recommendations for handling during assembly and/or disassembly.

   e. Drafted storm and sewer systems on Y-12 area map to facilitate establishment of sampling stations.

   f. Initiated study of safety of proposed HCP recycle system in 9204-3.

   g. Approved 9212 evacuation and storage procedures.

   h. Reviewed calculation methods for alpha emitters as applied to air contamination tests.

   i. Attended meeting relative to gathering meterological data for Y-12 area in conjunction with disaster plan.

   j. Investigated chip recovery dry-box for 9212.

   k. Started accumulation of data to determine possibility of fission assay of consumer parts, utilizing available equipment.

   l. Initial film and pen calibrations started using new calibration stand and 4.77 mg. radium source.

   m. Advised on film damage from Ra Br in 9204-3 equipment.

3. Critical Mass Experiments

   The Special Hazards Group furnished three man-days per week to the Critical Mass experimental program concentrating on the following items.

a. Further study was made on the suppression effect of stainless steel by comparison against aluminum.

b. Some time was also spent in an attempt to decontaminate certain building areas.

c. Recovery of material from hold-up as salvage was continued.

Other experiments are planned using a 10" aluminum cylinder and 15" and 20" stainless steel reactors. These cylinders are now being fabricated.

4. Other Projects

a. Continued study of special problem for Chemical Group at request of K. B. Brown.

b. Studied and discussed local Interaction Theory as contrasted with Los Alamos Theory.

c. Furnished further information with regard to measurement of enhancement of K-40 isotope.

SECTION II: HEALTH PHYSICS

1. Radiation Surveys

a. Personnel Monitoring

(1) Hand Counts

Four (4) Alpha Hand Counters have been installed in Bldg. 9212, i.e., one in each of the four wings. Hand Score Cards for each employee are provided in racks alongside each counter for purposes of recording a minimum of two hand counts daily.

A total of 2720 hand counts were recorded during the period of which total 44.5% were above the 500 d/minute tolerance level. These recorded counts ranged from background to > 10,000 c/min. which is slightly in excess of 500 d/M on the counter used. While hand contamination in this building is generally improved, much improvement is still to be desired and our efforts will continue toward that end.

(2) Film Monitoring

A film badge and pocket chamber calibration plate has been fabricated and procedures for their calibration have been set up. A new Weston Densitometer has also been received through the AEC Instrument Branch, which together with new film badges, pocket chambers and minometers provides the minimum essentials for personnel monitoring needs. A "gadget" designed to assemble film pads has been improved to the extent that it now works so that that need can now be said to be satisfied.

[redacted]

While the machine shops have been getting ready for operations and while we have awaited the procurement of the above-mentioned equipment, a system of personnel exposure records has been devised and is about to be inaugurated.

Until such time as additional coverage is indicated, presonnel in the following locations will be required to wear personnel monitoring equipment:

Bldg. 9731	- X-Ray Spectrograph
Bldg. 9212(Wing D)	- Radiography Shack
Bldg. 9203	- Counting Room
Bldg. 9766	- "Metal" Machine Shop
Bldg. 9212	- "Metal" Machine Shop

b. Air Survey

A total of one hundred fifteen (115) air samples were taken during the period. Nineteen (19) above-tolerance concentrations were obtained at the following locations:

(1) Bldg. 9212

(a) Room 44D - (Green Salt Conversion) Two above-tolerance samples predicted the need for a slight change of procedure in dry box operations.

(b) Room 52A - (Dumping Green Salt from Ball Mill) The gauntlet gloves, as provided in the original design, are now in use.

(2) Bldg. 9206

(a) Room # 6 - (Salvage Room) The operators are required to wear respiratory protective equipment.

(b) Room # 32 - (Peroxide Precipitation Process) Five (5) above-tolerance concentrations out of a total of 15 were obtained. Operators are required to wear respirators while performing this operation.

(c) Room # 51 - (Vapor Phase Chlorination) Four (4) above-tolerance concentrations were obtained out of a total of 12 samples taken. Operators are required to wear respirators.

(3) Bldg. 9204-3

(a) Major Repair Area - (Assembly of Receivers) Two (2) above-tolerance concentrations were obtained out of a total of six samples taken. Operations are intermittent.

(4) Bldg. 9733-3

(a) Room # 14 - (Sample Ball Milling and Grinding) One (1) above-tolerance concentration was obtained out of a total of 8 samples taken. Operators are required to wear respirators.

[redacted]

c. Water Surveys

The results of four (4) potable water samples continue to indicate that drinking water in this area is not contaminated.

The analytical results of the storm sewer samples taken during the past six weeks (one per week) have not yet been received.

2. Special Surveys

a. Radiography Shop

The study of radiation hazards within this building has been hampered by lack of good equipment, viz., a densitometer. Now that a densitometer has been received, it is hoped that this study can be completed within the next period.

b. Element 61 Spectrographic Analysis

A sample of Element 61 was brought in from Oak Ridge National Laboratories for analysis in the X-Ray Spectrograph. The target was loaded at X-10 and brought to this area in a ½" thick glass tube. Special precautions were taken, i.e., shielding and measurements, during the handling of this sample so as to provide more than adequate protection.

c. Radiation Checks for Shipment of Property

Three hundred and eighty (380) lots of equipment were checked for alpha, beta and/or gamma activity in accordance with Standard Practice Procedure #20A for release of property for shipment from Y-12.

3. Radiation Monitoring Instruments

a. Alpha Hand Counters. Three were completed, tested and calibrated after which they were installed in Bldg. 9212.

b. Beta, Gamma Hand Foot Counter. Construction is complete and the instrument is now being tested and calibrated.

c. Victoreen Minometer. Three 0.2 r. minometers were received during the period.

d. Walkie-Poppy. The first of three of these instruments has been completed and is now in use.

e. Beta Survey Meter. Instrument Development has designed and constructed a portable G-M tube (Mica Window) survey meter for use in making area surface checks.

f. Higginbotham Scaler and G-M Tube (Mica Window) Probe. Instrument Development has completed the construction of this instrument and a probe was procured from Oak Ridge National Laboratories. It is planned to use this instrument for checking contamination of clothing.

[redacted]

4. Personnel

Two (2) additional people were hired during the period, one of whom is now a member of the group, viz., R. W. Brothers. Management has indicated approval of further expansion and efforts to that end are now in process.

Following is a list of Department Personnel.

J. D. McLendon
J. W. Morfitt
R. L. Murray
E. G. Struxness

Others participating in the radiation measurement program are:

Instrument Development:

R. L. Quinn
E. L. Olson

Instrument Repair and Calibration:

J. H. Campbell
V. Lovett

Shipment Surveys:

R. W. Brothers
J. H. Hackney

Raymond Murray
Y-12 Special Hazards Group

EGStruxness
JWMorfitt

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Y/DZ-234
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Y-12

OAK RIDGE
Y-12
PLANT

MARTIN MARIETTA

Recycle and Biodestruction of Hazardous Nitrate Wastes

J. M. Napier
F. E. Kosinski

Chemistry and Chemical Engineering
Y-12 Development Division

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operated by
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for the
U.S. Department of Energy
under contract DE-AC05-84OR21400

#962

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MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Y/DZ-234
PREPRINT

Recycle and Biodestruction of Hazardous Nitrate Wastes

J. M. Napier
F. E. Kosinski

Development Division
Oak Ridge Y-12 Plant*
Martin Marietta Energy Systems, Inc.
Oak Ridge, Tennessee 37831

ABSTRACT

The U.S. Department of Energy (DOE) owns the Oak Ridge Y-12 Plant located in Oak Ridge, Tennessee. The plant is operated for DOE by Martin Marietta Energy Systems, Inc. One of the plant's functions involves the purification and recycling of uranium wastes. The uranium recycle operation uses nitric acid in a solvent extraction purification process, and a waste stream containing nitric acid and other impurities is generated.

Before 1976 the wastes were discarded into four unlined percolation ponds. In 1976, processes were developed and installed to recycle 50% of the wastes and to biologically decompose the rest of the nitrates. In 1983 process development studies began for in situ treatment of the four percolation ponds, and the ponds were treated and discharged by May 1986. The treatment processes involved neutralization and precipitation to remove metallic impurities, followed by anaerobic denitrification to reduce the 40,000 ug/g nitrate concentration to less than 50 ug/g. The final steps included flocculation and filtration. Approximately 10 million gallons of water in the ponds were treated and discharged.

* Operated for the U.S. Department of Energy by Martin Marietta Energy Systems, INc., under contract DE-AC05-84OR21400.

Introduction

The major responsibilities of the plant are: (1) producing weapon components and supporting DOE's design laboratories, (2) processing special materials, (3) supporting other DOE Oak Ridge Operations installations, and (4) supporting other U.S. agencies. The Y-12 Plant is within the city limits of the City of Oak Ridge and has several environmental challenges, all of which are being actively addressed. One of the challenges is the treatment and disposal of nitrate-rich liquids from a uranium recycle facility.

The plant uses a liquid-liquid solvent extraction process for purification and recycle of nonirradiated uranium wastes. One of the principal reagents is nitric acid, which is used to dissolve some of the uranium wastes. Since 1954, waste solutions from the solvent extraction process have been pumped into four unlined surface ponds. The ponds had no surface overflow; evaporation and percolation prevented the acidic wastes from overflowing the tops of the ponds.

In the past 20 years, many environmental laws have been enacted by the federal and state governments restricting the discharge of wastes to the air, water, and land. The continued use of open, unlined ponds for discharge of liquid wastes was essentially banned by the U.S. Congress by criteria established in the amended Clean Water Act of 1977. In anticipation of the future environmental restrictions, a management decision was made in 1971 by the Y-12 Plant and DOE to develop processes for recycling some nitrate wastes from the uranium purification process. It was also agreed that a process would be developed to biologically destroy some of the nitrate wastes. The remaining plant wastes from other operations were not recyclable and were to be discharged into the ponds until another disposal process could be developed.

Recycle Processes

The overall recycle process diagram is shown in Figure 1. Laboratory tests indicated that 30% of the nitrates could be recycled as nitric acid and 35% could be recycled as aluminum nitrate. The remaining nitrate (35%) could be biologically destroyed in a stirred-tank denitrification process.

The nitric acid waste comes from condensates produced in evaporation processes within the Y-12 Plant. The waste stream contains 3 to 10 wt % nitric acid, and the major impurities are approximately 100 mg/L of chlorides, 100 mg/L of fluorides, and 300 to 1000 mg/L of organics. To recycle the waste, the chlorides and fluorides have to be removed. The waste is passed through a vaporizer containing a mixture of 23.8 wt % aluminum nitrate nonahydrate, 53.9 wt % calcium nitrate tetrahydrate, and 23.3 wt % water (which removes the fluoride ions, as well as vaporizing the feed to the distillation column).

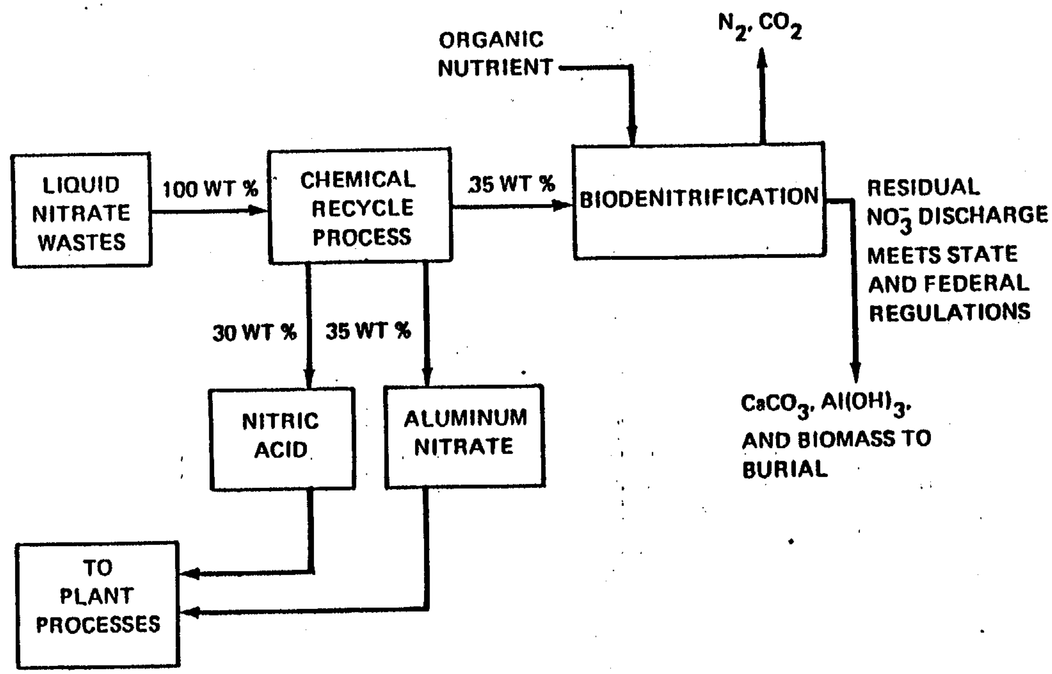

Fig. 1. PROCESS FLOW DESCRIPTION.

The vaporized salts are replaced when a 5:1 aluminum-to-fluoride weight ratio is obtained.

The dilute nitric acid vapors are then put into a glass distillation column where they are concentrated to 35 wt % nitric acid. The overhead distillate form the column is controlled at less than 50 mg/L of nitrates and is discharged to the environment at a pH of 6 to 9. The 35 wt % nitric acid product contains chloride and organic ions. The column is capable of producing 60 wt % acid, but because a reaction of the 60% acid with the organics can occur, a product of only 35 wt % acid was made.

The 35 wt % acid is batch treated with ozone to remove the chlorides to less than 10 mg/L. Most of the organics are also removed by the ozonation step. The purity of the recovered acid is usually better than commercially available acid.

A second waste, called raffinate, is a mixture of aluminum nitrate, free nitric acid, water, and all of the impurities extracted from the uranium solvent extraction process. The raffinate waste is vacuum heated at 60°C, and most of the free nitric acid is removed as condensate. This condensate is returned to the nitric acid distillation column and the acid is recycled to the plant. The vacuum-heated raffinate is cooled to 30°C and half of the aluminum nitrate is recycled to the plant. The rest of the nitrates are biologically decomposed in a stirred-tank reactor.

A review has been recently completed of these two recycle systems, which have operated satisfactorily since 1976. As a result of the review, a second distillation column has been installed that will serve as a backup to the original column. The amounts of recycled aluminum nitrate are also being increased from 50 to 70 wt %. No significant purity problems are expected to be encountered with the aluminum nitrate using the 70 wt % recycle level. These process changes should significantly increase the quantities of recycled nitrates from a nominal 65% to nearly 90%.

Stirred-Tank Bioreactor

As stated previously, the wastes from the aluminum nitrate recycle process are sent to a stirred-tank denitrification process. A stirred-tank design was chosen because the wastes contained high levels of calcium and aluminum salts that would plug a column denitrifier. An organic feed (calcium acetate) is used in the process. Several organics were initially investigated, but calcium acetate was selected. One of the reaction products is calcium carbonate. The nitrate waste feed contains about 3 wt % free nitric acid, which is not neutralized before injecting it into the bioreactor. The acid is neutralized by the calcium carbonate within the bioreactor.

The stirred-tank solution contains 50 mg/L of nitrates, 93 wt % water, and 7 wt % solids. The dried solids typically contain 45% calcium carbonate, 45% aluminum hydroxide, and 10% biomass, plus trace quantities of metallic oxides and hydroxides.

The stirred tanks have performed satisfactorily since 1976, and denitrification rates up to 5 g of nitrate per liter of reactor solutions per day are common. This denitrification rate means that a nominal 475 g (1045 lbs) of nitrate ions are decomposed each operating day into a 95,000-L (25,000-gal) stirred reactor. To sustain this rate, process conditions must be controlled. The carbon-to-nitrogen (C/N) weight ratio is maintained at 1:1 to 1:2. The solution pH in the tank must be above 6.8 and below 9.0. The soluble phosphate ions must be 5 to 100 mg/L. The dissolved oxygen has to be below 2 mg/L and the temperature above 10°C. The stirred tank solution is relatively easy to control since the incoming feed flow rate is small as compared to the volume of the tank (nominal 20- to 30-day liquid retention time).

The liquid and solid wastes from the bioreactor are used to neutralize other acid wastes and to seed the bioreactors, which is discussed in the next section.

Denitrification of Four Ponds

As previously stated, some of the Y-12 Plant's wastes were not recyclable and were discharged to the four open ponds. The installation of the recycle and stirred-tank processes in 1976 significantly decreased the nitric acid flows to the ponds. In 1983, a decision was made to stop discharging wastes into the ponds and to develop a process to treat the acid waters in the ponds.

Laboratory tests were made and a denitrification reactor was successfully operated in an open container. Batch tests using volumes up to 208 L (55 gal) were denitried at rates up to 1000 mg NO_3 per day per liter of reactor solution.

A pond chosen as a pilot plant had an initial nitrate level of 8300 mg/L and a pH of 2.7. The other ponds had nitrate levels up to 44,000 mg/L, and all were at pH 2.7 or below. The process steps used for the in situ treatment of the pond are listed in Table 1. In order to stir the pond, two large pumps (8000-L/min pumping capacity) were installed to gently stir the ponds. The pond was neutralized by adding calcium carbonate to a pH of 5 and then sodium hydroxide and calcium hydroxide to obtain a pH of 7. The organic carbon was added to the pond as acetic acid, which was also neutralized when the pond was neutralized. Bacteria from the stirred-tank reactors were added to seed the pond. The mixing pumps were operated to keep the bacteria in suspension but not at a stirring rate fast enough to inject large amounts of air (oxygen) into the water.

TABLE 1

Treatment Process for the Four Unlined Ponds

Process Steps

1. Neutralization
2. Organic carbon addition
3. Bacteria
4. Denitrification
5. Aeration (bio-oxidation of excess carbon)
6. Solids removal
    - Settling of Solids
    - Flocculation
    - Filtration
    - Storage
7. Release of water

After denitrification, the water was aerated by using floating aerators to biologically decompose the excess organic carbon that was added to ensure that all of the nitrates were biologically destroyed. The pumps were then stopped, and most of the solids settled. The water was pumped from the ponds to a ferric hydroxide flocculation process, filtered, and released. The water was chlorinated before flocculation to remove algae that had grown in the ponds after denitrification was complete.

The results of the pilot test are shown in Figure 2. As noted, all of the nitrates were destroyed in fewer than 38 days. About 14 of the 38 days were not useful because the pH of the pond was low and no denitrification occurred. During denitrification, the temperature and other process parameters were monitored. The other three ponds were then denitrified, and data on one of the other ponds are shown in Figure 3. Cold water interrupted the reaction for about two months. When the ambient temperature increased by about 10°C, the reaction restarted and continued until a low pH was achieved. Low pH conditions were common because acetic acid was injected at various times into the pond to adjust the C/N ratio. The denitrification reaction also forms carbon dioxide gas (carbonic acid), which lowers the pH. As noted in the data, a nominal denitrification rate of 300 mg of NO_3 per day per liter of pond solution was experienced. This rate is equal to decomposition of 2270 g of nitrates per day (5000 lbs/day) per pond.

The ponds were then aerated, using floating aerators, and the excess organic carbon was decomposed. Most of the solids were then allowed to settle in the ponds. However, algae formed in the water and had to be removed by chlorination before discharge to the environment. The water was then flocculated via ferric hydroxide and filtered to remove the total suspended solids to less than the discharge limit of 60 mg/L. The water was processed through the flocculation process and discharged at rates up to 200 L/min (60 g/min.) The ponds are now empty and the solids remain in the bottom of the empty ponds. The solids will be stored until a final decision has been reached concerning their disposition.

The water of the water being discharged to the environment was regularly monitored, and some of the data are shown in Tables 2 and 3. As noted, the quality was signficantly purer than required by the U.S. Environmental Protection Agency National Pollutant Discharge Elimination System (NPDES) permit.

Future Wastes

As previously mentioned, one of the program goals was to develop treatment processes for future wastes. A series of steel tanks (2,000,000-l volume) was installed as treatment reactors. The acid wastes were neutralized with calcium hydroxide and put into one of

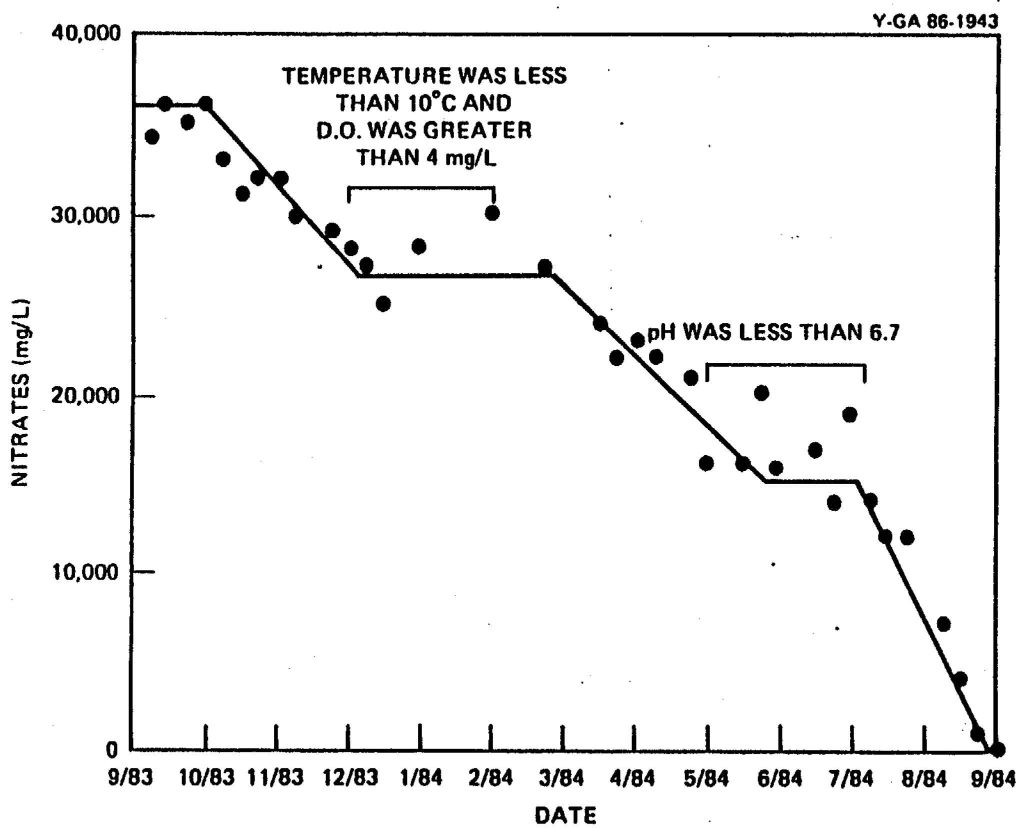

Fig. 2. NITRATE CONCENTRATION, NORTHWEST POND.

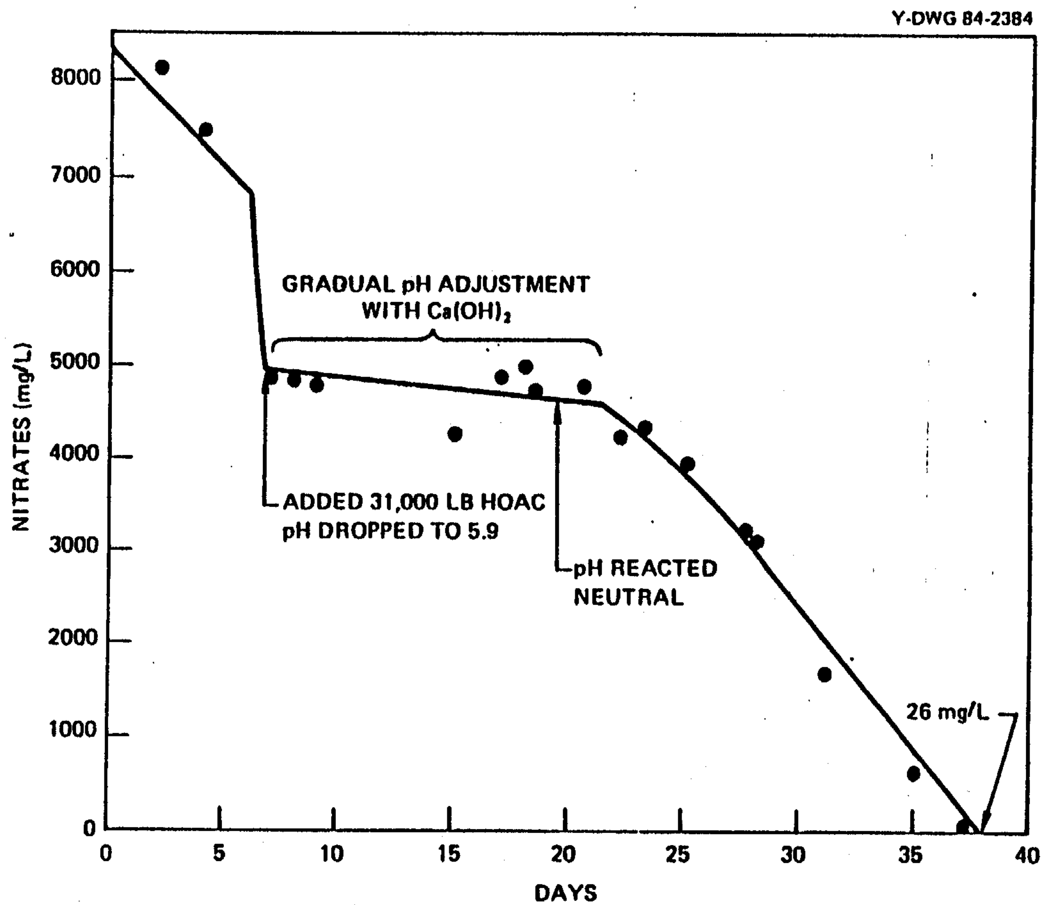

Fig. 3. NITRATE CONCENTRATION, SOUTHEAST POND.

TABLE 2

Contaminants	Original Pond (mg/L)	Treated Water (mg/L)	NPDES (a) Permit Limits Daily Max (mg/L)
Ag	0.006	0.02	0.43
Ca	0.23	0.002	0.69
Cn	-	0.002	1.20
Cr	4.8	0.01	2.77
Cu	5.6	0.01	3.38
Ni	31.3	0.08	3.98
Pb	2	0.01	0.69
Zn	4.25	0.13	2.61
Total Toxic Organics	-	0.33	2.13
Total Suspended Solids			
Oil and Grease	-	2.6	52
pH	2	7 to 8	6 to 9

(a) National Pollutant Discharge Elimination System.

TABLE 3

Other Pond Contaminant Concentration

Contaminants	Original Pond (mg/L)	Treated Water (mg/L)
As	0.14	.06
Al	583	0.15
Hg	-	0.002
Be	0.06	0.001
SO_4	-	3725
Ba	0.27	0.2
F	-	4.2
Ca	847	478
Cl	-	0.96
NO_3	8300 to 44,000	6

Note: Biological tests were required.

the stirred tanks. Acetic acid and biomass were added to the tank. Very high denitrification rates (up to about 4000 mg of NO_3 per day per liter are common. A tank is usually decomposed in less than 90 days at a beginning nitrate level of 45,000 mg NO_3 per liter. The water and solids are then flocculated, and the solids are stored in a steel tank until a decision is made on the final discharge process for the solids. The treated water must meet the same chemical specifications for release to the environment as required for the ponds, plus two biological tests. The biological tests include survival of four-day-old fathead minnows for seven days and a seven-day test with ceriodaphnia. The ceriodaphnia must reproduce, and the reproduction rate must be equal to the control test group.

Conclusion

The recycle processes are operating and some of the wastes are being recycled. The waste ponds are now empty and will not be reused. The new process tanks are operating satisfactorily, and all future wastes will be batch treated and released. The water quality will meet the chemical and biological specifications.

Distribution

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